Chemical bond approach to the electric susceptibility of semiconductors. II

R. N. Nucho, J. G. Ramos,* and P. A. Wolff
Department of Physics, Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 8 August 1977)

The method previously developed to relate chemical bonds to the dielectric constant of elemental semiconductors is extended to the ionic tetrahedral III-V compounds. Expressions for the static dielectric constant and the average optical gap in terms of the generalized Wannier functions for the valence bands are obtained. Only two parameters are needed. The first is a measure of the antibonding character of the valence bands and the second is related to the ionic nature of these compounds. We have allowed the former to vary from compound to compound, while we have set the latter at a predetermined constant value, as prescribed by Coulson. We separate the energy gap into two analytical parts, "homopolar" and "heteropolar," thus directly confirming the ionicity scale established by Phillips. Finally, Coulson's definition of ionicity is reconciled with that of Phillips.

I. INTRODUCTION

In a recent paper[1] (I), we have developed a dielectric theory of bonding in covalent semiconductors. Our approach, in contrast to other theories[2-6] of this type, does not require a specific model for the electron Hamiltonian. Instead, we base our theory on the relative sharpness of the dielectric function $[\epsilon_2(\omega)]$, and use this feature to derive (via a moment expansion) a relation between the static dielectric constant and the valence-band Wannier functions for the column-IV semiconductors. This approach makes possible a nearly first-principles calculation of $\epsilon_1(0)$, which is accurate to about 10%, and confirms the general expression for $\epsilon_1(0)$ used by Phillips.[3]

In the present paper, we analyze the III-V semiconductors using this method. Here, the new feature is the ionic character of these compounds. As indicated by Phillips,[4] the definition of ionicity is not unique. We start by following Coulson's approach,[4,7] in which the bonding combination of orbitals (i.e., the valence-band Wannier functions for covalent semiconductors) become asymmetric mixtures of orbitals. This approach, as we shall see, is the natural one for us to choose. We then proceed to calculate the dielectric constant and the optical gap and show that we can separate the average gap into two parts, a covalent (or homopolar) one and an ionic (or heteropolar) one, in a straightforward manner. This procedure parallels that of Phillips and enables us to justify his well-known ionicity scale.[3] We show, further, that the two definitions of ionicity, as given by Coulson on one hand and Phillips on the other, are *not* contradictory, but that in fact, starting from one definition, we can reproduce the other.

In this work, two parameters are needed. The first is similar to the parameter introduced in I and describes the antibonding character of the valence bands. The second arises from the ionic nature of the III-V semiconductors and is related to Coulson's ionicity. This parameter, according to Coulson's prescription, has a fixed value for all the III-V compounds.

A brief review of our formalism is given in Sec. II and the necessary modifications for the ionic tetrahedral semiconductors are discussed in Sec. III. In Sec. IV we derive expressions for the dielectric constant and the average energy gaps, and Sec. V is devoted to a discussion of Phillips' work and to the confirmation of his ionicity scale.

II. REVIEW OF THE FORMALISM

In this section, we outline briefly the steps that led to a general expression for the static dielectric constant in terms of chemical bonds, as discussed in I. Our starting point was the Kramers-Kronig relation at $\omega = 0$,

$$\epsilon_1(0) = 1 + \frac{2}{\pi}\int_0^\infty \frac{\epsilon_2(\omega)}{\omega}\, d\omega . \tag{1}$$

Taking advantage of the steep δ-functionlike character of $\epsilon_2(\omega)$, we expanded the quantity $1/\omega$ about an average frequency $\overline{\omega}$ which we subsequently determined by setting the second term in the corresponding expansion of $\epsilon_1(0) - 1$ identically equal to zero. Our final result for $\epsilon_1(0)$ could then be written [see Eq. (6b) of I]

$$\epsilon_1(0) = 1 + (\omega_p^2/\overline{\omega}^2)D , \tag{2}$$

where ω_p is the valence-electron plasma frequency, D is a dimensionless factor of order unity, accounting for the effect of high-lying core d states, and

$$\bar{\omega} = \int \omega \epsilon_2(\omega) d\omega \Big/ \int \epsilon_2(\omega) d\omega$$

$$= \frac{\pi}{2} \left(\omega_p^2 \Big/ \int \epsilon_2(\omega) d\omega \right). \tag{3}$$

In deriving Eq. (3), three approximations were made. First, all core excitations were neglected because they occur at high energies and do not contribute significantly to $\epsilon_1(0)$, due to the factor $1/\omega$ in Eq. (1). Secondly, the last term in our expansion for $\epsilon_1(0)$ [see Eq. (5) of I] was dropped, imposing a fundamental error of about 10% on our theory. Finally, during the evaluation of the factor D, as described in Sec. V of I, we neglected transitions between valence electrons and very high conduction bands, for the same reason we neglected core excitations, namely, that they occur at high energies.

Referring to Eq. (2), we see that it confirms the expression of Phillips.[3] $\bar{\omega}$ is proportional to the first moment of $\epsilon_2(\omega)$ and we interpret it as a mean optical gap, whereas $\bar{\omega}_{\text{Phillips}}$ corresponds to the position of the resonance of the $\epsilon_2(\omega)$ curve. Since ω_p is known, the problem is reduced to a calculation of the integral $\int \epsilon_2(\omega) d\omega$. Substituting the standard form for $\epsilon_2(\omega)$ in terms of position matrix elements into this integral, using completeness to eliminate the conduction bands, and transforming to a localized basis, we found [Eq. (19) of I],

$$\int \epsilon_2(\omega) d\omega = \frac{8\pi^2 e^2}{V\hbar} \left(\sum_{ij} \langle ij | \hat{\epsilon} \cdot \vec{r} |^2 | ij \rangle - \sum_{\substack{ii' \\ jj'}} | \langle ij | \hat{\epsilon} \circ \vec{r} | i'j' \rangle |^2 \right), \tag{4}$$

where i and j are quantum numbers which specify a complete set of valence-band states. The remaining problem was to find adequate localized functions to use in this expression. We discussed this issue at length in our earlier work where we considered a general tight-binding framework. For simplicity, we used a Hamiltonian of the Hall-Weaire type to calculate our generalized Wannier function for the valence band of group-IV semiconductors. The justification for using such a Hamiltonian was discussed, and we only quote here our results [Eq. (18b) of I]

$$a_j^v(\vec{r} - \vec{R}_i) = \frac{1}{(1+6\gamma^2)^{1/2}} \left[\phi_j^b(\vec{r} - \vec{R}_i) + \gamma \left(\sum_{j' \neq j} \phi_{j'}^a(\vec{r} - \vec{R}_i) - \sum_{j' \neq j} \phi_{j'}^a(\vec{r} - \vec{R}_i - \vec{\delta}_j + \vec{\delta}_{j'}) \right) \right], \tag{5}$$

where $\vec{\delta}_j$ is the nearest-neighbor vector joining atom I to atom II along the j direction and $\phi_j^a(\vec{r} - \vec{R}_i)$ and $\phi_j^b(\vec{r} - \vec{R}_i)$ are, respectively, purely antibonding and purely bonding combinations of the two sp^3 hybrids, ψ_j^{I} and ψ_j^{II}, along bond j at site i. In the Hall-Weaire model, γ is a parameter which determines the amount of antibonding character in the valence-band Wannier function. $\gamma = \frac{1}{4}(V_1/V_2)$ if the overlap S of the two hybrids forming a bond is neglected, and $\gamma = \frac{1}{4}(M_1/M_2)\sqrt{1-S^2}$ if $S \neq 0$, where

$$\begin{bmatrix} V_2 \\ M_2 \end{bmatrix} = \langle \psi_j^{\mathrm{I}}(\vec{r} - \vec{R}_i) | H | \psi_j^{\mathrm{II}}(\vec{r} - \vec{R}_i - \vec{\delta}_j) \rangle$$

$$= \langle \psi_j^{\mathrm{II}}(\vec{r} - \vec{R}_i - \vec{\delta}_j) | H | \psi_j^{\mathrm{I}}(\vec{r} - \vec{R}_i) \rangle \tag{6}$$

$$\begin{bmatrix} V_1 \\ M_1 \end{bmatrix} = \langle \psi_j^{\mathrm{I}}(\vec{r} - \vec{R}_i) | H | \psi_{j'}^{\mathrm{I}}(\vec{r} - \vec{R}_i) \rangle$$

$$= \langle \psi_j^{\mathrm{II}}(\vec{r} - \vec{R}_i - \vec{\delta}_1) | H | \psi_{j'}^{\mathrm{II}}(\vec{r} - \vec{R}_i - \vec{\delta}_1) \rangle, \quad (j \neq j').$$

The upper matrix elements are to be used if the sp^3 hybrids do not overlap and the lower ones if they do. Our notation, throughout, is the same as that chosen in I.

The above completes the survey of our basic formalism. We must now adapt the previous results to the case of the III-V semiconductors.

III. MODIFICATIONS FOR THE III-V SEMICONDUCTORS

In this section we extend the calculation of the dielectric constant, as described in Sec. II and in I, to the partially ionic, tetrahedrally bonded III-V semiconductors such as GaAs. The new feature which we must account for here is the ionic character of these compounds. Since we have been using bonding and antibonding combinations of sp^3 atomic hybrids in constructing our valence-band Wannier functions, it is natural in the ionic case for us to introduce the concept of ionicity via Coulson's definition[7] which essentially concentrates the valence electrons around one type of atom, in the primitive cell, rather than equally around both types, as in the case of the group-IV semiconductors. Neglecting overlap, it is known[4] that

$$\phi_j^b(\vec{r} - \vec{R}_i) = \frac{1}{(1+\lambda^2)^{1/2}} [\psi_j^{\mathrm{I}}(\vec{r} - \vec{R}_i) + \lambda \psi_j^{\mathrm{II}}(\vec{r} - \vec{R}_i - \vec{\delta}_j)], \tag{7a}$$

$$\phi_j^a(\vec{r}-\vec{R}_i)=\frac{1}{(1+\lambda^2)^{1/2}}[\lambda\psi_j^{\mathrm{I}}(\vec{r}-\vec{R}_i)-\psi_j^{\mathrm{II}}(\vec{r}-\vec{R}_i-\vec{\delta}_j)], \tag{7b}$$

where $\lambda^2/(1+\lambda^2)$ is the probability of the electron being around atom II and is related to Coulson's ionicity f_C by the following equation

$$f_C=\frac{1-\lambda^2}{1+\lambda^2}. \tag{8}$$

Equation (8) is the difference between the probabilities of the electron being on atoms I and II. The wave functions in Eqs. (7) diagonalize the simplest tight-binding Hamiltonian, which not only includes the coupling (V_2) between every two hybrids forming a bond, as in the case of the elemental semiconductors, but must also account for the fact that the hybrid energies are now different for the two atoms in the primitive cell. This energy difference, which we denote by $2V_I$, is the source of the parameter λ. We choose $2V_I=\epsilon^a-\epsilon^c$ to be a negative quantity. The superscript a refers to the anion (atom I) and c refers to the cation (atom II). Note that Harrison[5] calls this quantity $-2V_3$. (In our notation, V_3 is one of the tight-binding parameters described in I and has nothing to do with V_I). λ is the first parameter of our theory for the ionic semiconductors. Coulson gives a prescription for calculating ionicity from the ionization energy and electron affinity. He finds the value $f_C=0.37$ for all III-V semiconductors.[4] By contrast, in the Phillips theory, the ionicity varies considerably within the III-V's. We will see presently that this difference has its origin in a different *definition* of ionicity. In fact, using a constant value of λ throughout the III-V's, we are able to reproduce Phillips' results without additional parameters. Thus, in the first phase of our work, λ will be a universal parameter which cannot be used to fit our results with experiment. To find how λ depends on V_I, we must proceed with the diagonalization of the simple Hamiltonian mentioned above. Using the hybrids as a basis set and spanning the crystal bond by bond, this Hamiltonian can be written, in matrix form, as follows:

$$H=\begin{array}{c} \\ \psi_j^{\mathrm{I}} \\ \psi_j^{\mathrm{II}} \\ \psi_{j'}^{\mathrm{I}} \\ \psi_{j'}^{\mathrm{II}} \\ \text{etc.} \\ \vdots \end{array}\begin{array}{c} \begin{array}{cccccc} \psi_j^{\mathrm{I}} & \psi_j^{\mathrm{II}} & \psi_{j'}^{\mathrm{I}} & \psi_{j'}^{\mathrm{II}} & & \text{etc...} \end{array} \\ \begin{bmatrix} V_I & V_2 & & & & \\ V_2 & -V_I & & 0 & & 0 \\ & & V_I & V_2 & & \\ & 0 & V_2 & -V_I & & 0 \\ & & & & & \\ 0 & & 0 & & & \text{etc...} \end{bmatrix} \end{array}. \tag{9}$$

We have chosen the reference energy for each bond to be at $\frac{1}{2}(\epsilon^a+\epsilon^c)$ for convenience. The Hamiltonian, as can be seen, is separable. Each block can be diagonalized independently, yielding bonding and antibonding states for each. The eigenvalues are separated by an energy difference $|\Delta|=2(V_2^2+V_I^2)^{1/2}$ and the eigenfunctions correspond to the antibonding and the bonding states given by Eqs. (7) with

$$\lambda=\left[1+\left(\frac{V_I}{V_2}\right)^2\right]^{1/2}-\frac{V_I}{V_2}. \tag{10}$$

Overlap makes the problem more complicated. The energy difference between the bonding and the antibonding eigenvalues then becomes

$$|\Delta|_{S\neq 0}=2[(M_2^2+M_I^2(1-S^2)]^{1/2}/(1-S^2), \tag{11}$$

where we have denoted by M_2 and M_I the matrix elements corresponding to V_2 and V_I, in the case $S\neq 0$ [see Eqs. (6) and Ref. 6]. It is easy to write down the form of one of the eigenfunctions, for instance the bonding one, in terms of λ and S, namely,

$$\phi_j^b(\vec{r}-\vec{R}_i)=(1+\lambda^2+2\lambda S)^{-1/2}\times[\psi_j^{\mathrm{I}}(\vec{r}-\vec{R}_i)+\lambda\psi_j^{\mathrm{II}}(\vec{r}-\vec{R}_i-\vec{\delta}_j)]. \tag{12a}$$

The antibonding eigenfunction can be obtained by constructing a function that is orthogonal to Eq. (12a). With the two conditions of orthogonality and normality, we obtain

$$\phi_j^a(\vec{r}-\vec{R}_i)=\frac{S+\lambda}{[(1-S^2)(1+\lambda^2+2\lambda S)]^{1/2}}\times\left(\psi_j^{\mathrm{I}}(\vec{r}-\vec{R}_i)-\frac{1+\lambda S}{S+\lambda}\psi_j^{\mathrm{II}}(\vec{r}-\vec{R}_i-\vec{\delta}_j)\right). \tag{12b}$$

It can be verified that Eqs. (12) diagonalize the Hamiltonian given in (9) with M's instead of V's and that

$$\lambda=-\{M_I+[M_2^2+M_I^2(1-S^2)]^{1/2}\}/(M_2+SM_I). \tag{13}$$

It must be remembered that the matrix elements M_I, M_2, and M_3 are all negative, thus yielding a positive value for λ. In the $S\neq 0$ case, λ relates to Coulson's ionicity via

$$f_C=(1-S)^{1/2}(1-\lambda^2)/(1+\lambda^2+2\lambda S). \tag{14}$$

This expression is explained in the Appendix.

From here on, the calculation proceeds exactly as in Sec. III of I and we can use our earlier result of Eq. (18a) to obtain the generalized Wannier function for the ionic semiconductors. The resulting expression is similar to Eq. (5) with ϕ^a

and ϕ^b given by the ionic functions in (12). Since, to our knowledge, there exist no values in the literature for the tight-binding parameters of the III-V semiconductors, obtained from a fit to the valence band, we shall consider γ as the second parameter of our theory. Physically, γ is a measure of the antibonding character of the valence band, or, equivalently, of the delocalization of the valence-band Wannier function. Unlike λ, γ is a variable quantity which we shall in fact determine from the experimental values of $\epsilon_1(0)$. However, we do know that γ will have a form similar to the one we derived previously for the group-IV elements, bearing in mind that the average energy separation between bonding and antibonding states, in this case, is given by Eq. (11). Thus, we can write, in analogy, for the ionic case

$$\gamma_{S=0} = \tfrac{1}{4}|V_1|/(V_2^2+V_I^2)^{1/2}, \qquad \gamma_{S\neq 0} = \tfrac{1}{4}|M_1|(1-S^2)^{1/2}/[M_2^2+M_I^2(1-S^2)]^{1/2}. \tag{15}$$

IV. DIELECTRIC CONSTANT AND OPTICAL GAP

Having determined the appropriate localized valence-band functions for the III-V semiconductors, we proceed with the calculation of Eq. (4). We shall use the wave functions $|ij\rangle = a_j^v(\vec{r}-\vec{R}_i)$ given by Eqs. (5), (12), and (15). The computation is similar to that of the group-IV elements. After some tedious algebra, we obtain the following result, to order γ^2:

$$\int \epsilon_2(\omega)d\omega = \frac{\pi m}{4\hbar}\omega_p^2(P-\gamma Q+\gamma^2 R), \tag{16}$$

where

$$P = \frac{1}{1+\lambda^2+2\lambda S}\sum_j\left[\langle r^2(j)\rangle_{\rm I}+\lambda^2\langle r^2(j)\rangle_{\rm II}+2\lambda\langle r^2(j)\rangle_{\rm ov}-\hat{\epsilon}\cdot\vec{\delta}_j[\langle r(j)\rangle_{\rm I}-\lambda^2\langle r(j)\rangle_{\rm II}]+(1+\lambda^2)\left(\frac{\hat{\epsilon}\cdot\vec{\delta}_j}{2}\right)^2\right]$$
$$-\frac{1}{(1+\lambda^2+2\lambda S)^2}\sum_j\left[\left(\langle r(j)\rangle_{\rm I}+\lambda^2\langle r(j)\rangle_{\rm II}-(1-\lambda^2)\frac{\hat{\epsilon}\cdot\vec{\delta}_j}{2}\right)^2+\sum_{j'\neq j}|\langle r(j,j')\rangle_{\rm I}|^2+\lambda^4\sum_{j'\neq j}|\langle r(j,j')\rangle_{\rm II}|^2\right],$$

$$Q = \frac{2(S+\lambda)}{(1-S^2)^{1/2}(1+\lambda^2+2\lambda S)}\sum_{j\neq j'}\left(-\langle r^2(j,j')\rangle_{\rm I}-\lambda\eta\langle r^2(j,j')\rangle_{\rm II}-\frac{2}{1+\lambda^2+2\lambda S}\hat{\epsilon}\cdot\vec{\delta}_j[\alpha\langle r(j,j')\rangle_{\rm I}+\beta\langle r(j,j')\rangle_{\rm II}]\right.$$
$$\left.+\frac{4}{1+\lambda^2+2\lambda S}[\langle r(j,j')\rangle_{\rm I}\langle r(j)\rangle_{\rm I}+\lambda^3\eta\langle r(j,j')\rangle_{\rm II}\langle r(j)\rangle_{\rm II}]\right),$$

$$R = -6P+\frac{2(S+\lambda)^2}{(1-S^2)(1+\lambda^2+2\lambda S)}\sum_j\left(3\langle r^2(j)\rangle_{\rm I}+3\eta^2\langle r^2(j)\rangle_{\rm II}-6\eta\langle r^2(j)\rangle_{\rm ov}-3\hat{\epsilon}\cdot\vec{\delta}_j[\langle r(j)\rangle_{\rm I}-\eta^2\langle r(j)\rangle_{\rm II}]\right.$$
$$+\sum_{j\neq j'}[\langle r^2(j,j')\rangle_{\rm I}+\eta^2\langle r^2(j,j')\rangle_{\rm II}]$$
$$\left.+\sum_{j\neq j'}\hat{\epsilon}\cdot\vec{\delta}_j[\langle r(j,j')\rangle_{\rm I}-\eta^2\langle r(j,j')\rangle_{\rm II}]+\tfrac{1}{4}[11(1+\eta^2)-16\eta S](\hat{\epsilon}\cdot\vec{\delta}_j)^2\right),$$

where

$$\eta = (1+S\lambda)/(S+\lambda), \quad \alpha = (\eta-3\lambda)\tfrac{1}{2}S+\lambda(\eta-\lambda), \quad \beta = \lambda[\eta(1-\lambda^2)+\tfrac{1}{2}\lambda S(\eta+\lambda)].$$

The computation, overall [i.e., Eq. (16)], is origin independent. However, once an origin is chosen, it must be used consistently throughout the calculation. The quantities appearing in Eq. (16) are defined in the following, where $\psi^{\rm I}$ and $\psi^{\rm II}$ stand for the sp^3 hybrids introduced before

$$S = \int \psi_j^{*\rm I}\left(\vec{r}_j+\frac{\vec{\delta}_j}{2}\right)\psi_j^{\rm II}\left(\vec{r}_j-\frac{\vec{\delta}_j}{2}\right)d^3r_j, \tag{17a}$$

$$\langle r^2(j)\rangle_{\rm ov} = \int \psi_j^{*\rm I}\left(\vec{r}_j+\frac{\vec{\delta}_j}{2}\right)(\hat{\epsilon}\cdot\vec{r}_j)^2\times\psi_j^{\rm II}\left(\vec{r}_j-\frac{\vec{\delta}_j}{2}\right)d^3r_j. \tag{17b}$$

For these two overlap integrals, the origin is at the center of bond j.

$$\langle r(j)\rangle_{\rm I} = \int \psi_j^{*\rm I}(\vec{r})(\hat{\epsilon}\cdot\vec{r})\psi_j^{\rm I}(\vec{r})d^3r, \tag{17c}$$

$$\langle r^2(j)\rangle_{\rm I} = \int \psi_j^{*\rm I}(\vec{r})(\hat{\epsilon}\cdot\vec{r})^2\psi_j^{\rm I}(\vec{r})d^3r, \tag{17d}$$

$$\langle r(j,j')\rangle_{\rm I} = \int \psi_j^{*\rm I}(\vec{r})(\hat{\epsilon}\cdot\vec{r})\psi_{j'}^{\rm I}(\vec{r})d^3r, \tag{17e}$$

$$\langle r^2(j,j')\rangle_{\rm I} = \int \psi_j^{*\rm I}(\vec{r})(\hat{\epsilon}\cdot\vec{r})^2\psi_{j'}^{\rm I}(\vec{r})d^3r, \tag{17f}$$

(and similar expressions with II instead of I.) The origin for these local integrals is at the site of atom I or II, as the case may be. The ionic calculation was more complicated than the nonionic one mainly because the inversion symmetry of the problem was lost. This new feature explains, for

TABLE I. Numerical results using best fit values for γ for the III-V semiconductors. Energies are in eV.

Element	$\epsilon_1(0)$ [a] (exper.)	γ	D [a]	$\hbar\bar{\omega}$ (theor.)	Experimental [b] peak in $\epsilon_2(\omega)$	$\sigma\gamma$	$\hbar\bar{\omega}_h$ [d] (theor.)	E_h [c] $/\sqrt{A}$	f [d] (theor.)	f_p [c]
AlP	8.5	0.152	1.00	6.03	···	0.167 0.173	5.28 5.16	5.02	0.234 0.269	0.307
AlAs	10.2	0.159	1.11	5.48	···	0.175 0.177	4.88 4.84	4.64	0.208 0.221	0.274
AlSb	10.2	0.142	1.19	4.97	4.25–4.60	0.156 0.167	4.53 4.35	3.73	0.171 0.237	0.250
GaP	9.1	0.150	1.11	6.12	5.27–5.74	0.165 0.176	5.36 5.13	5.03	0.233 0.295	0.327
GaAs	10.9	0.156	1.23	5.51	4.85–5.33	0.172 0.179	4.91 4.78	4.59	0.205 0.248	0.310
GaSb	14.4	0.172	1.33	4.38	4.1 –4.5	0.189 0.191	4.01 3.97	3.75	0.161 0.175	0.261
InP	9.6	0.147	1.19	5.50	4.8 –5.1	0.162 0.181	4.73 4.39	4.19	0.261 0.364	0.421
InAs	12.3	0.160	1.33	4.86	4.5 –5.0	0.176 0.189	4.26 4.03	3.90	0.232 0.311	0.357
InSb	15.7	0.174	1.42	3.96	4.08	0.191 0.202	3.57 3.40	3.26	0.187 0.263	0.321

[a] Reference 10.
[b] Reference 3, p. 169.
[c] Reference 3, p. 42.
[d] Two sets of results are given. The upper numbers result from our theory with $\lambda = 0.5$. The lower numbers result from using Harrison's corrections in our theory.

instance, the appearance of the second bracket in P, which comes from both the diagonal and off-diagonal parts of the second term of Eq. (4). Whereas previously we could neglect this quantity, it represents about 10% of P in the ionic case and must be retained. However, these new terms are still relatively small, and the main contribution to Eq. (4) comes from the first term of that equation. We calculated the overlap S and found that it presented only small deviations from the average value of 0.53 from compound to compound. We chose the value 0.50, as before.

A word is in order about the validity of the Herman-Skillman orbitals[8] in the ionic calculation. These orbitals were derived for neutral atoms, and consequently, are certainly not a good description of the physical situation if there is a large charge transfer from the cation to the anion. An estimate of the effective charge transfer may be obtained by studying the interaction of the dynamical lattice optical and longitudinal modes with an electromagnetic field. The results, as quoted in Ref. 3, p. 85, indicate, for the III-V semiconductors, that the lattice acts as if only about $\frac{1}{5}$ of an electron were transferred from the cation to the anion. This argument strongly suggests the adequacy of the Herman-Skillman orbitals for our calculation.

From the dielectric constant data, we calculated the energy gaps via Eq. (2). In turn, the energy gaps yielded the values of our parameter γ, with the help of the following relation, obtained from Eqs. (3) and (16)

$$\bar{\omega} = \frac{2\hbar/m}{P - \gamma Q + \gamma^2 R} . \tag{18}$$

Our numerical results are presented in Table I, and are discussed in Sec. VI.

V. HOMOPOLAR GAP AND IONICITY

In this section we wish to relate to the work done by Phillips on the subject of ionicity. We first present a brief overview of some of his work[3,4] and then show how our theory confirms his ionicity scale, which was established on a semiempirical basis.

Phillips starts by separating the crystal potential into even and odd parts with respect to interchange of the two atoms in the primitive cell, the origin being chosen at the center of bond, as follows:

$$V(\vec{r}) = \sum_{\alpha} V_A(\vec{r} - \vec{R}_\alpha) + \sum_{\beta} V_B(\vec{r} - \vec{R}_\beta)$$

$$= \sum_{G} V(G) e^{i\vec{G}\cdot\vec{r}} .$$

$\vec{R}_\alpha$ and $\vec{R}_\beta$ label the sublattices of A and B atoms, respectively, and $\vec{G}$ is a reciprocal-lattice vector in the usual Fourier expansion. Here

$$V_G = \frac{1}{\Omega} \int_{\text{primitive cell}} V(r) e^{-i\vec{G}\cdot\vec{r}}\, d^3r$$

$$= \frac{1}{\Omega} \int [V_A(\vec{r} - \vec{R}_A) + V_B(\vec{r} - \vec{R}_B)] e^{-i\vec{G}\cdot\vec{r}}\, d^3r$$

$$= \frac{1}{\Omega} \sum_{G'} [V_A(G') e^{-i\vec{G}'\cdot\vec{R}_A} + V_B(G') e^{-i\vec{G}'\cdot\vec{R}_B}] \int e^{i(\vec{G}'-\vec{G})\cdot\vec{r}}\, d^3r = V_A(G) e^{i\vec{G}\cdot(\vec{R}_B-\vec{R}_A)/2} + V_B(G) e^{-i\vec{G}\cdot(\vec{R}_B-\vec{R}_A)/2}$$

$$= [V_A(G) + V_B(G)] \cos\left(\vec{G}\cdot\frac{\vec{R}_B - \vec{R}_A}{2}\right) + i[V_A(G) - V_B(G)] \sin\left(\vec{G}\cdot\frac{\vec{R}_B - \vec{R}_A}{2}\right), \tag{19}$$

where we have used the relation

$$\int e^{i(\vec{G}'-\vec{G})\cdot\vec{r}}\, d^3r = (2\pi)^3 \delta(\vec{G} - \vec{G}'),$$

and, have factored out the quantity $\exp[-i\vec{G}\cdot\frac{1}{2}(\vec{R}_B + \vec{R}_A)] = 1$. Phillips then shows that a potential of the form of Eq. (19), between real basis functions, will yield off-diagonal matrix elements of the type $E_h + iC$. It follows that the energy difference between the bonding and antibonding states, or energy gap, will be

$$E_g^2 = E_h^2 + C^2 . \tag{20}$$

E_h is the "homopolar" gap and arises from the symmetric part of the potential, while C represents the ionic contribution and arises from the antisymmetric part. Equation (20) lends itself to a natural definition of ionicity, namely,

$$f_P = C^2/E_g^2 = 1 - E_h^2/E_g^2 . \tag{21}$$

Phillips' prescription for calculating f_P combines Eqs. (20) and (21) with the expression for the static dielectric constant obtained from the isotropic Penn model[9]

$$\epsilon_1(0) = 1 + [(\hbar\omega_p)^2/E_g^2] A D , \tag{22}$$

where ω_p is the valence-electron frequency, D is the core-correction factor calculated by Van Vechten,[10] and the quantity $A = 1 - E_g/4E_F$ arises from the spreading of the bands near E_g, the Penn gap. E_F refers to the Fermi energy of the electrons. For the group-IV semiconductors, the potential is symmetric with respect to interchange of atoms A and B, and $E_g = E_h$. From the data for $\epsilon_1(0)$, Phillips establishes, empirically, via Eq. (22) a power law form for E_h, depending only on bond length d:

$$E_h = \alpha d^{-2.5} , \tag{23}$$

where the coefficient α is taken to be a constant. He then extrapolates this law to the ionic $A^N B^{8-N}$ compounds to obtain the corresponding values of E_h. From the dielectric constant data and Eq. (22), once again, he obtains the values of the total gaps, and in turn, via Eq. (20), the corresponding values of C. Once C and E_h are known, the ionicity scale is established.

Let us now consider the form we determined for our energy gap [see Eq. (18)]. This quantity was calculated using wave functions that were essentially bonding in character, of the form $\phi_A + \lambda\phi_B$. If we now set $\lambda = 1$, this wave function becomes symmetric with respect to interchange of atoms A and B. Thus, it would be reasonable to expect, if we set $\lambda = 1$ in our generalized Wannier function and repeat our preceding calculation, that we should obtain a "homopolar" gap comparable to that of Phillips. Consequently, we define, by analogy to Eq. (18),

$$\overline{\omega}_h = \frac{2\hbar/m}{P - \gamma Q + \gamma^2 R|_{\lambda=1}} . \tag{24}$$

In this calculation, it is important to note that not only are the numerical values of P, Q, and R different than in the preceding one, but so is γ (see Table II). We can find the change in γ by examining Eqs. (13) and (15). Observing that setting $\lambda = 1$ is equivalent to setting $M_I = 0$, we can write

$$\gamma_{\lambda=1} = \frac{1}{4}\frac{M_1}{M_2}(1 - S^2)^{1/2} = \gamma_{\lambda\neq1}\left[1 + \left(\frac{M_I}{M_2}\right)^2 (1 - S^2)\right]^{1/2}$$

$$= \sigma\gamma_{\lambda\neq1} . \tag{25}$$

From Eq. (13) we can find M_I/M_2 in terms of λ and thus obtain

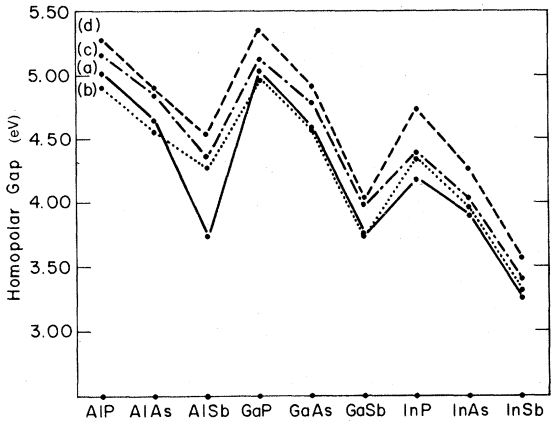

FIG. 1. Homopolar gaps for the III-V semiconductors (eV): (a) Phillips; (b) present theory with $\lambda = 0.31$; (c) present theory with $\lambda = 0.50$ and values of σ from Harrison; (d) present theory with $\lambda = 0.50$.

$$\sigma = (1 + \lambda^2 + 2\lambda S)/(2\lambda + S + \lambda^2 S). \tag{26a}$$

Alternatively, we can express σ in terms of the zero overlap parameters

$$\sigma = [1 + (V_I/V_2)^2]^{1/2}. \tag{26b}$$

In obtaining this form we have used the relations[6] $V_2 = M_2/(1 - S^2)$ and $V_I = M_I/(1 - S^2)^{1/2}$ which can be found by equating Eq. (11) to its zero overlap value, $2(V_2^2 + V_I^2)^{1/2}$.

Our numerical results are given in Table I, and are discussed in Sec. VI. The values we predict for E_h and f_P are plotted against those of Phillips

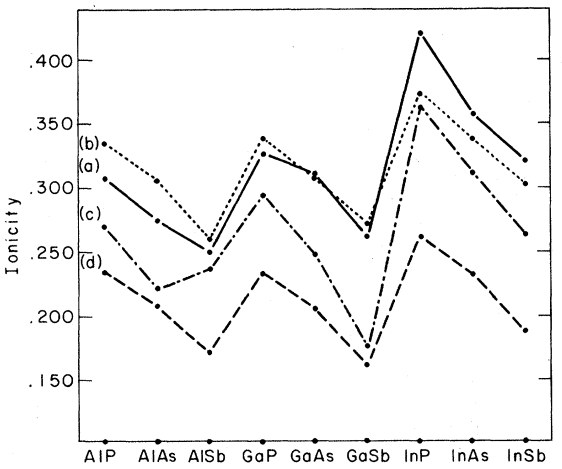

FIG. 2. Ionicity scale for the III-V semiconductors: (a) Phillips; (b) Present theory with $\lambda = 0.31$; (c) Present theory with $\lambda = 0.50$ and values of σ from Harrison; (d) Present theory with $\lambda = 0.50$.

in Figs. 1 and 2 [curves a], with which they are in good agreement. We have calculated two sets of numbers. One set corresponds to values of γ corrected according to Eq. (26a) using Coulson's ionicity [see curve d], and the other corresponds to values of γ corrected according to Eq. (26b) using the V_I/V_2 ratios tabulated by Harrison[5] (V_3/V_2 in his notation) [see curve c].

VI. CONCLUSION

Examining Table I, we observe that, apart from the case of AlSb, the values of γ generally show the same "metallic" trend in descending the Periodic Table which we established in paper I for the elemental semiconductors. The generalized Wannier function becomes more delocalized as one approaches the lower compounds. The energy gaps $\hbar\bar{\omega}$ compare well with the experimental peaks of $\epsilon_2(\omega)$, and the predicted homopolar gaps, $\hbar\bar{\omega}_h$, lie within 10% of those given by Phillips (again excepting AlSb) (see Fig. 1).

Assuming no antibonding mixing, the gaps obtained are too large, as we found in the group-IV case, yielding results for $\epsilon_1(0)$ that are 30%–45% too low. Considering AlP, GaAs, and InSb, for example, these gaps are, respectively, 7.55, 6.94, and 5.94 eV. Had we used these gaps in our calculation for $\epsilon_1(0)$, we would have had to introduce, again, a factor similar to that of Harrison (see I) in order to obtain good correspondence between theory and experiment. The values of this correction factor would have been, respectively, 1.25, 1.26, and 1.39 compared to those quoted by Harrison and Pantelides[11] which are 1.07, 1.24, and 1.47.

As for the ionicity scale, the behavior indicated by our theory correlates well with that described by Phillips, although we would obtain better results with larger values of σ, as can be seen from curve (c) in Fig. 2 obtained from Harrison's values ($\sigma \simeq 1.2$) as compared to ours ($\sigma \simeq 1.1$) in curve d. Examining Eq. (26a), we observe that larger values of σ correspond to smaller values for λ (in the range $0 < \lambda < 1$). We conclude from these observations that setting λ equal to a constant does describe the ionic trend of the III-V semiconductors as described by Phillips and that his *relative differences* in ionicity are mainly due to the size of the s and p orbitals surrounding the atoms. *Absolute values* of ionicity, on the other hand, are determined by the magnitude of λ. Our analysis indicates that smaller values of λ, corresponding to larger values of Coulson's ionicity [see Eq. (14)], will improve the agreement between our curve and that of Phillips considerably. Indeed, choosing $\lambda = 0.31$, which corresponds to a value of Coulson's ionicity of

TABLE II. Numerical results of our theory with $\lambda = 0.31$.

Element	γ	$\sigma\gamma$	$\hbar\bar{\omega}_h$ (theor.)	f (theor.)
AlP	0.154	0.185	4.91	0.336
AlAs	0.159	0.191	4.56	0.306
AlSb	0.142	0.171	4.28	0.260
GaP	0.153	0.184	4.97	0.339
GaAs	0.157	0.189	4.58	0.308
GaSb	0.170	0.205	3.74	0.271
InP	0.152	0.183	4.35	0.374
InAs	0.161	0.194	3.95	0.339
InSb	0.173	0.208	3.31	0.302

about 0.56, we arrived at an almost exact fit for GaAs and a much better fit overall, as shown by Table II and curves b of Figs. 1 and 2. We have thus been able to relate Coulson's definition of ionicity to that of Phillips. Coulson's ionicity measures, to a first approximation, how much static charge has been transferred to the anion, while the Phillips', on the other hand, measures how "ionic" or how "asymmetric" the gap is. We have shown that assuming a constant charge transfer for the III-V semiconductors is consistent with the Phillips description which we have found to depend mainly on the size of the atomic orbitals.

ACKNOWLEDGMENTS

This work was supported by the U. S. Air Force Office of Scientific Research, Air Force Systems Command under Contract/Grant AFOSR-76-2894. One of us (J.G.R.) was supported in part by a FAPESP (Brazil) fellowship.

APPENDIX: EFFECT OF OVERLAP ON IONICITY

First, we note that λ, as given by Eq. (10) may be written as follows:

$$\lambda = \left[1 + \left(\frac{V_I}{V_2}\right)^2\right]^{1/2} - \frac{V_I}{V_2} = \left(\frac{1 + V_I/(V_2^2 + V_I^2)^{1/2}}{1 - V_I/(V_2^2 + V_I^2)^{1/2}}\right)^{1/2}.$$

Referring to the work of Harrison,[5] we see that this is precisely,

$$\lambda = [(1 - \alpha_p)/(1 + \alpha_p)]^{1/2},$$

where $\alpha_p = |V_I|/(V_2^2 + V_I^2)^{1/2}$ is defined by Harrison as the parameter representing polarity.

Calculating Coulson's ionicity via Eq. (8), we find

$$f_C = (1 - \lambda^2)/(1 + \lambda^2) = \alpha_p .$$

Thus, Coulson's ionicity is identical, by definition, to Harrison's polarity. These results are valid for the zero overlap case. To find the relation between f_C and λ for the $S \neq 0$ case, we refer to the work of Harrison and Ciraci[6] in which they calculate α_p in terms of the wave function coefficients. Thus, comparing our expression (12a) with Eqs. (13) and (14) of Ref. 6, we can make the following identifications:

$$u_a^2 = \frac{1}{2}\left(\frac{1 - S(1 - \alpha_p^2)^{1/2}}{1 - S^2} + \frac{\alpha_p}{(1 - S^2)^{1/2}}\right) = \frac{1}{1 + \lambda^2 + 2\lambda S},$$

$$u_c^2 = \frac{1}{2}\left(\frac{1 - S(1 - \alpha_p^2)^{1/2}}{1 - S^2} - \frac{\alpha_p}{(1 - S^2)^{1/2}}\right) = \frac{\lambda^2}{1 + \lambda^2 + 2\lambda S}.$$

We can calculate α_p as a function of λ from either of these equations. After some algebra, we obtain the solution which is consistent with both equations, namely,

$$\alpha_p = (1 - S^2)^{1/2}(1 - \lambda^2)/(1 + \lambda^2 + 2\lambda S).$$

Making the identification $\alpha_p = f_C$, we obtain Eq. (14).

---

*On leave of absence from Instituto de Fisica "Gleb Wataghin", Universidade Estadual de Campinas, Campinas, SP, Brazil.

[1]R. N. Nucho, J. G. Ramos, and P. A. Wolff, Phys. Rev. B 17, 1843 (1978).
[2]D. Weaire and M. F. Thorpe, Phys. Rev. B 4, 2508 (1971).
[3]J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).
[4]J. C. Phillips, Rev. Mod. Phys. 42, 317 (1970).
[5]W. A. Harrison, Phys. Rev. B 8, 4487 (1973).
[6]W. A. Harrison and S. Ciraci, Phys. Rev. B 10, 1516 (1974).
[7]C. A. Coulson, L. R. Redei, and D. Stocker, Proc. R. Soc. Lond. 270, 357 (1962).
[8]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, 1963).
[9]D. R. Penn, Phys. Rev. 128, 2093 (1962).
[10]J. A. Van Vechten, Phys. Rev. 182, 891 (1969) and Ref. 1.
[11]W. A. Harrison and S. T. Pantelides, Phys. Rev. B 14, 691 (1976).